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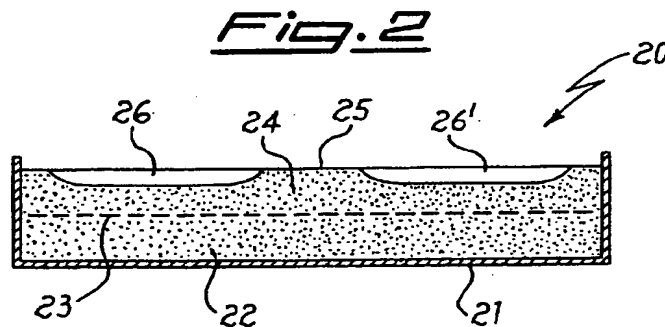
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(54) **Frittable evaporable getter device having a high yield of barium**

(57) An evaporable getter device that can be frit sealed is described, being capable of releasing barium quantities of at least 300 mg for the use in picture tubes of traditional type or flat displays. The device comprises a container (21) in which there is a mixture of powdered

BaAl<sub>4</sub> alloy and nickel, in the form of a packet at the upper surface of which there is a variable number of radial recesses (26,26'); a discontinuous metallic member (23) is provided within the packet.



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## Description

The present invention relates to a "frittable" evaporable getter device with a high yield of barium. As is known, the evaporable getter materials are mainly employed for the maintenance of vacuum at the inside of picture tubes for television sets and of computer screens. The use of evaporable getter materials at the inside of flat displays, being at present in a developing stage, is also under study.

The getter material being commonly used in picture tubes is the metallic barium which is deposited in the form of a thin film on an inner wall of the tube. To obtain this film use is made of devices, known in the field as evaporable getter devices, which are introduced in the tube during its manufacturing. These devices comprise a open metallic container innerly comprising powders of a compound of barium and aluminum,  $\text{BaAl}_4$ , and powders of nickel, Ni, in a ratio by weight of about 1:1. Barium is caused to evaporate by induction heating the device by means of a coil at the outside of the picture tube itself, in an activation process also defined as "flash"; when the temperature in the powders reaches a value of about 800°C, the following reaction takes place:



This reaction is strongly exothermic and raises the temperature of the powders to about 1200°C, at which barium evaporation occurs; barium vapors then sublimate onto the walls of the tube to form the metallic film. Evaporable getter devices are well known in the technique; for example US Patent No. 5.118.988 in the applicant's name, discloses getter devices in which some recesses are formed at the free surface of the packet of powders for retarding heat propagation within the packet in a circumferential direction, thus allowing a controlled barium flash. US Patent 3.558.962 discloses a getter device in which a metallic element, preferably a wire net, is immersed in the packet of powders in a generic position with the purpose of rendering more uniform the temperature at the inside of the packet of powders.

The processes for the manufacture of picture tubes, both of the traditional and of the flat type, involve a step of welding to each other two glass portions, that is carried out in a so-called "frit sealing" operation, by causing a glass paste with a melting temperature of about 450°C to be molten or softened between the two portions in the presence of air. In the traditional picture tubes a getter device may be introduced after the frit sealing through the neck provided for housing the electronic gun; however in this case the size of the getter device is conditioned by the neck diameter and the precise positioning of the device within the picture tube is difficult. On the other hand in case of flat displays, it is practically impossible to position the getter device after the frit sealing step. Consequently the manufacturers of picture tubes have an increasing tendency to the insertion of the getter device before the frit sealing. During the frit sealing step, the getter device is exposed, at a temperature of about 450°C, to the atmospheric gases and the vapors released by the low-melting glass paste. The main result is the surface oxidation of nickel. During barium flash, nickel oxide gives rise with aluminum to a strongly exothermic reaction, hardly controllable: this may lead to the raising of the packet of powders, the ejection of the chips therefrom or the partial melting of the container, thus being detrimental to the correct operation of the getter device and of the tube as a whole. These problems could theoretically be overcome by supplying the device with less power during the flash operation; this would lead to a more controlled barium evaporation, but with a longer evaporation time, which cannot be accepted in the industry of picture tubes.

Evaporable getter devices which can withstand frit sealing without alterations, or however without causing the above-described drawbacks, are defined as "frittable".

Frittable getter devices are already manufactured and sold by the applicant. These devices can be manufactured with traditional technologies as long as some critical values are not exceeded: in particular it is impossible to go beyond certain given thicknesses of the packet of powders, because with too great thicknesses the quantity of heat generated in the body of the packet of powders is dissipated only slowly, thus giving rise to problems as described above. It has been found empirically that the ratio between the quantity of barium comprised in the device, given in mg, and the device diameter, given in mm, must not be more than about 10. Due to reasons relating to the manufacturing of picture tubes, the maximum possible diameter of the getter devices is of about 20 mm, so that the maximum quantity of barium that can be evaporated from frittable getter devices manufactured with traditional technologies is of about 200 mg. However the picture tubes of big size require quantities of evaporated barium of at least 300 mg and such a demand cannot be met by frittable devices according to the prior art. Frittable getter devices capable of evaporating barium quantities of more than 200 mg will be defined, in the following part of description and in the claims, as of the "high yield type".

Even by resorting to prior art solutions, which allow to obtain excellent results in case of non frittable getter devices, it is impossible to obtain frittable getter devices with a high yield: in fact, by making radial recesses on the surface of the packet of powders as described in the mentioned US Patent 5.118.988, the operation of barium evaporation after frit sealing causes however the swelling of the packet itself or the ejection of chips therefrom. In the devices according to the US Patent 3.558.962 a metallic member, preferably a wire net, is immersed in the packet of powders in a generic position. There is described the case in which the net is in contact with the container bottom or even welded on the bottom itself or compressed in the free surface of the packet of powders. Also in this case both these positions of the net

do not allow to obtain frittable getter devices, giving rise to the problems as described above.

The production of frittable getter devices without dimensional limits, and consequently of high yield devices, is the object of various patents.

US Patent 4.127.361, owned by the applicant, discloses getter devices which can be made frittable by means of a protective layer of organo-silanes; in spite of its efficiency, this covering process is too slow and thereby unacceptable for an industrial production.

US Patent 4.342.662 and JP Hei 2-6185 Patent, both assigned to Toshiba, disclose evaporable getter devices which are frittable (in the following also simply defined as frittable getter devices) obtained by covering, the whole packet of powders with a glass-like film of boron oxide containing up to 7% of silicon oxide, or respectively only nickel with a glass-like film of boron oxide only. The manufacturing of these devices is however difficult, because the film must have a controlled and reproducible thickness.

Object of the present invention is that of providing an evaporable getter device which is free of the drawbacks of the prior art.

According to the present invention this object is achieved with a frittable evaporable getter device with a high yield of barium comprising:

- a metallic container open at the top;
- a mixture of powders of  $BaAl_4$  and nickel in the container, formed as a packet on the upper surface of which radial recesses are provided;
- a discontinuous metallic member of essentially planar shape and essentially parallel to the container bottom; characterized in that the metallic member is immersed in the powders packet in a position spaced apart from the container bottom and such as not to emerge at the free surface of the packet itself.

The invention will be described in the following with reference to the drawings in which:

- Fig. 1 shows some possible embodiments of discontinuous metallic members which can be used in the devices of the invention;
- Figg.2-6 show cutaway sectional views of some possible embodiments of getter devices according to the invention.

For the purposes of the invention it is necessary that a metallic member is immersed in the packet of powders at such a position to be spaced apart from the bottom and not to emerge at the surface. As a matter of fact the induction heating of the getter device mainly occurs by virtue of the container and the metal member immersed in the powder, which thereafter transfer heat to the getter material powders. It has been observed that in the areas of contact between the metal member and the container bottom the heat transfer to the powders is scarcely efficient and a local overheating takes place; if these contact areas are too many or excessively extended, the non-dissipated heat causes the packet of powders to raise and in some cases parts of the device to melt. On the contrary if the metallic member emerges at the free surface of the packet, the surface itself is subdivided in areas which are poorly bound one to another and during the flash are subject to be ejected within the picture tube.

The metallic member can be made of various metals, such as iron alloys, nickel alloys or aluminum alloys; preferred is the use of steel AISI 304 for its easy cold workability.

The metal member can have different shapes, provided it is discontinuous and essentially planar.

The condition of discontinuity is necessary because the member will not obstruct the release of barium vapours produced in the portion of powders between the member itself and the container bottom. This condition can be obtained through the most different geometrical shapes. Some possible embodiments are shown in fig.1: for example, the metal member may be formed as a metallic cut blank having a rayed shape, like the element 10 in the drawing, showing a central hole for helping the release of barium from the underlying powders; it may be a cut blank showing a multiplicity of holes distributed on the surface either in a random or in an orderly way, as exemplified by the member 12; or it may be a wire net as described in the mentioned US Patent 3.558.962.

The member must be essentially flat to be able to be immersed in the packet of powders, which generally has a thickness of few millimeters, without contacting the container bottom and without coming out from the surface of the powders. The condition that the metallic member must not be in contact with the bottom of the container can be obtained in various ways. Some embodiments are shown in figures 2-6, wherein various metallic members are represented in correspondence with various methods employed to keep them at a distance from the bottom, but each of the various types of member (ray-shaped cut blank, holed blank, wire net or others) can be used in each one of the configurations described in the following. A possible getter device of the invention is shown in cross-section in figure 2; such a device 20 is obtained by pouring onto the bottom of the container 21 a first portion 22 of powders, laying on the upper surface thereof a flat metallic member 23 and covering the latter with the remainder portion 24 of powders. Finally the powders are compressed in the container with a shaped punch so that on the upper surface 25 of the packet radial

recesses 26,26'... are formed. The ratio by weight between the quantity of powders placed in the container before and after the positioning of the metallic member 23 determines the level of the same member within said packet and therefore it is chosen in such a way that the member will not emerge on the surface 25 not even where the recesses 26,26'... are located; good results are in general obtained when such a ratio is comprised between about 1:2 and 1:3. In another possible embodiment, as exemplified in fig.3a, the metallic member 33 can be deformed locally thus obtaining thereon some "feet" 34; as shown in figure 3b representing in cross-section a getter device 30 according to the invention, when the member 33 is placed in the container 31 wherein the powders 32 are present, the feet 34 keep it at a pre-set distance from the bottom 35 of the container. Also in this case on the upper surface 36 of the packet of powders there are the radial recesses 37,37',..... Again, as exemplified in fig.4 showing in cross-section another possible getter device 40 of the invention, it is possible to obtain deformations 44 in the side walls 45 of container 41, in which powders 42 are present, and lay the metallic member 43 on deformations 44; at the upper surface 46 of the packet of powders there are formed the recesses 47, 47',..... Finally, as exemplified in fig.5 showing in cross-section still another possible getter device 50 according to the invention, it is possible to obtain elevations 54 on the bottom 55 of container 51 comprising the powders 52, whereby supports are formed on which the metallic member can rest; also in this case at the upper surface 56 of the packet of powders there are formed recesses 57, 57',..... This latter possibility is preferred in case that a container is used having elements of mechanical anchoring of the packet of powders as described in the US Patent 4.642.516 and shown in fig.6: in this case, in fact, the metallic member 63 can be merely a flat one and resting on these elements of mechanical anchoring 64. In those cases as exemplified in figs.2-6 the position and the size of deformations, both of container and of the metallic member, determine the position of the latter and are defined in such a way that it does not emerge at the upper surface of the packet of powders, not even where the radial recesses are located.

The container of the device according to the invention may be anyone among the containers of the prior art. This is generally made of steel, preferably of the type AISI 304 or 305, for its easy cold workability by pressing and good resistance to the oxidizing conditions during the operation of frit sealing of the picture tube. The shape of said container is essentially that of a short cylinder, closed in the bottom and open at the top, although various modifications of this basic shape are possible, such as e.g. the deformations of the bottom or of the side walls as previously described.

The packet of powders is comprised of a mixture of powdered  $\text{BaAl}_4$  of powdered nickel. The particle size of the powders of  $\text{BaAl}_4$  is generally lower than about  $250\text{ }\mu\text{m}$ ; the particle size of the powders of nickel is generally lower than about  $60\text{ }\mu\text{m}$ . The ratio by weight between the two materials is generally between about 1.2:1 and 1:1.2; preferably this ratio by weight is of about 1:1. The packet of powders is formed locally by pouring a mixture of loose powders in the container and pressing the same by suitable punches. At the upper surface of the packet some recesses are formed in radial direction, in a varying number from 2 to 8, as described in the mentioned US Patent no. 5.118.988.

The devices of the invention may also be produced in a nitrogen-containing version: it is known in the field the use of getter devices containing small quantities of nitrogen compounds, such as iron nitride,  $\text{Fe}_4\text{N}$ , germanium nitride,  $\text{Ge}_3\text{N}_4$  or intermediate nitrides of iron and germanium. The purpose of these components is that of generating small pressures of nitrogen in the picture tube during the step of barium flash, thus allowing to obtain more extended and uniform deposits of barium.

The invention will be further illustrated by the following examples. These non-limiting examples show some embodiments designed to teach those skilled in the art how to practice the invention and to represent the best considered mode for putting into practice the invention.

#### EXAMPLE 1

A getter device is prepared by using a container of steel AISI 304 having diameter of 20 mm and height of 4 mm with the bottom shaped with elevations 1 mm high like those shown in fig.5. Within the container there is positioned a net of steel AISI 304 with meshes of 1,5 mm width, resting on the bottom elevations. A homogeneous mixture is poured into the container, being comprised of 775 mg of powdered  $\text{BaAl}_4$ , for a total content of 403 mg of barium, and 875 mg of powdered nickel. The mixture of powders is then compressed at the inside of the container with a punch so shaped as to form at the surface of packet 4 radial recesses. The sample thus obtained is treated at  $450^\circ\text{C}$  during 1 hour in air to simulate the frit sealing conditions. The sample is then placed in a glass flask being connected to a pump system, the flask is evacuated and a barium evaporation test is carried out by following the method described in the standard ASTM F 111-72 while heating the device by means of radio frequencies for 35 s with such a power that the evaporation starts 15 s after the heating begins. The result of the test is reported in Table 1, in which there are indicated notes on the evaporation details, the aspect of the remainder and the quantity of evaporated barium.

#### EXAMPLE 2

The test of example 1 is repeated with a mixture including a nitrogen dispenser, formed of 785 mg of powdered nickel, 825 mg of powdered  $\text{BaAl}_4$  and 40 mg of  $\text{Fe}_4\text{N}$ . The results of the test are reported in Table 1.

**(COMPARATIVE) EXAMPLE 3**

The test of example 1 is repeated, but without adding the wire net in the packet of powders. The results of the test are reported in Table 1.

**(COMPARATIVE) EXAMPLE 4**

The test of example 1 is repeated, but by using for compressing the powders in the container a flat punch, so that the surface of the packet does not show radial recesses. The results of the test are reported in Table 1.

**(COMPARATIVE) EXAMPLE 5**

The test of example 1 is repeated, but using a container with flat bottom and causing the wirenet to rest on the bottom thereof. The results of the test are reported in Table 1.

**(COMPARATIVE) EXAMPLE 6**

The test of example 1 is repeated, but using a sample in which the net emerges at the surface of the packet of powders: this sample has been obtained by pouring the mixture of powders into the container, laying the net upon the powders and compressing the whole by means of a flat punch. The results of the test are reported in Table 1.

Table 1

EXAMPLE	NOTES
1	Intact packet; intact container; evaporated barium: 300 mg.
2	Intact packet; intact container; evaporated barium: 330 mg.
3	Ejection of the packet of powders; evaporated barium: non detectable.
4	Remarkable central swelling of the packet of powders; evaporated barium: 300mg.
5	Melting of the container; evaporated barium: non detectable.
6	Ejection of chips from the surface of the packet of powders; evaporated barium: non detectable.

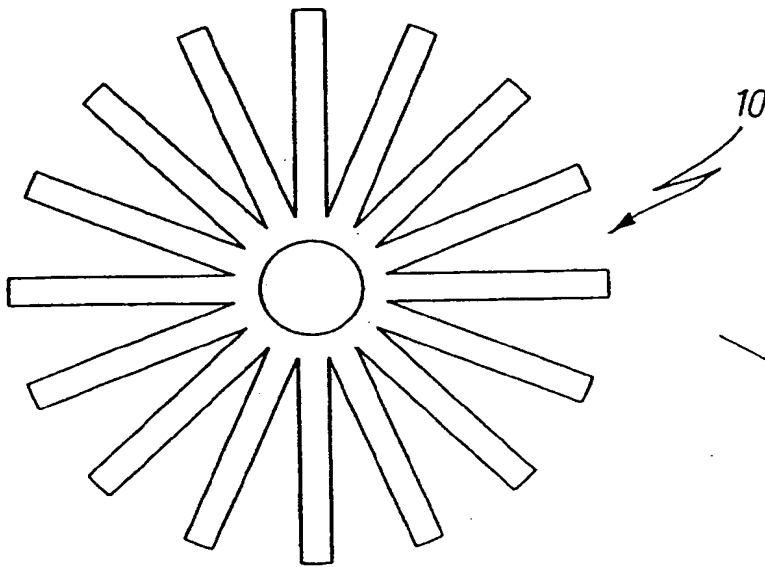
As it is appreciated from the results in the Table, only the devices according to the invention (examples 1 and 2) appear to be fritttable, since they do not show problems relating to the swelling or ejection of the packet of powders or to the container melting; in addition these devices allow to obtain a yield of barium of 300 mg or more. On the contrary with all the other devices there are problems of swelling or ejection of the powders, in full or partially, or even the melting of the whole device occurs.

**Claims****1. Fritttable evaporable getter device with high yield of barium comprising:**

- a metallic container open at the top;
  - a mixture of powdered  $BaAl_4$  and nickel in the container in the form of a packet on the upper surface of which there are formed radial recesses;
  - a discontinuous metallic member of essentially planar shape and essentially parallel to the bottom of the container;
- characterized in that the metallic member is immersed in the packet of powders at a position spaced apart from the bottom of the container, such as not to emerge at the free surface of the packet itself.

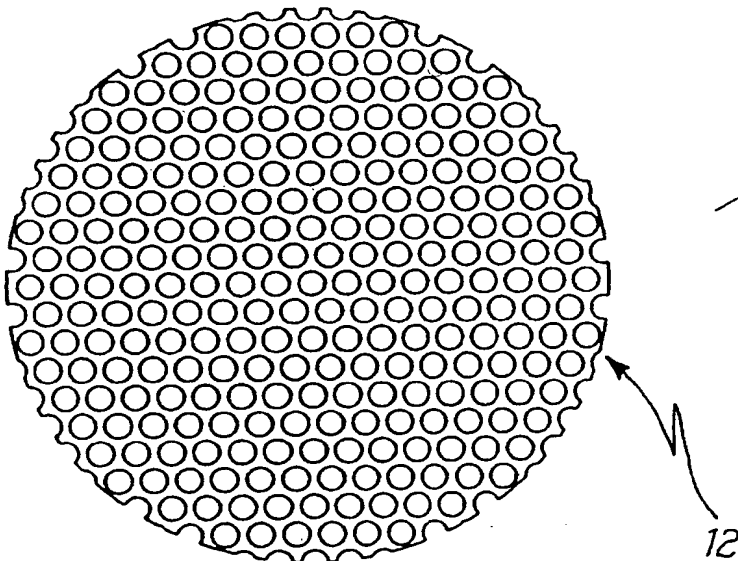
**2. A device according to claim 1, in which the metallic member immersed in the packet of powders is formed as a metallic cut blank (10) having a rayed shape.****3. A device according to claim 1 in which the metallic member immersed in the packet of powders is formed as a cut blank (12) showing a multiplicity of holes distributed on its surface.**

4. A device according to claim 1 in which the metallic member immersed in the packet of powders is formed as a wire net.
5. A device (20) according to claim 1, comprising an upperly open container (21); a first portion (22) of the packet of powdered  $\text{BaAl}_4$  and nickel on the bottom of the container; a flat metallic member (23) placed on the first portion of powders and covered with the remainder portion (24) of the packet of powdered  $\text{BaAl}_4$  and nickel; radial recesses (26,26',...) on the upper surface (25) of the packet of powders.
6. A device (30) according to claim 1, comprising an upperly open container (31); a packet (32) of powdered  $\text{BaAl}_4$  and nickel inserted in the container; a metallic member (33) with local deformations shaped as feet (34) immersed in the packet of powders so that the feet are in contact with the bottom (35) of the container; radial recesses (36,36',...) on the upper surface (37) of the packet of powders.
7. A device (40) according to claim 1, comprising an upperly open container (41) with deformations (44) on the side walls (45); a packet (42) of powdered  $\text{BaAl}_4$  and nickel in the container; a flat metallic member (43) supported by the deformations; radial recesses (47,47',...) at the upper surface (46) of the packet of powders.
8. A device (50) according to claim 1, comprising an upperly open container (51) on the bottom (55) of which there are elevations (54); a packet (52) of powdered  $\text{BaAl}_4$  and nickel in the container; a flat metallic member (53) resting on the elevations; radial recesses (57, 57',...) on the upper surface (56) of the packet of powders.
9. A device according to claim 8, in which the elevations on the container bottom have a circular shape (64).
10. A device according to claim 1, in which the powders of  $\text{BaAl}_4$  have a particle size of less than  $250\text{ }\mu\text{m}$ .
11. A device according to claim 1, in which the powders of nickel have a particle size of less than  $60\text{ }\mu\text{m}$ .
12. A device according to claim 1, in which the powders of  $\text{BaAl}_4$  and nickel are present in a ratio by weight comprised between about 1.2:1 and 1:1.2.
13. A device according to claim 12, in which the powders of  $\text{BaAl}_4$  and nickel are present in a ratio by weight of about 1:1.
14. A device according to claim 1, in which the recesses at the surface of the packet of powders are in a number between 2 and 8.
15. A device according to claim 1, in which the mixture of powders also comprises a nitrogen dispenser compound chosen among iron nitride, germanium nitride or intermediate nitrides of iron and germanium.



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Fig. 1



12

Fig. 2

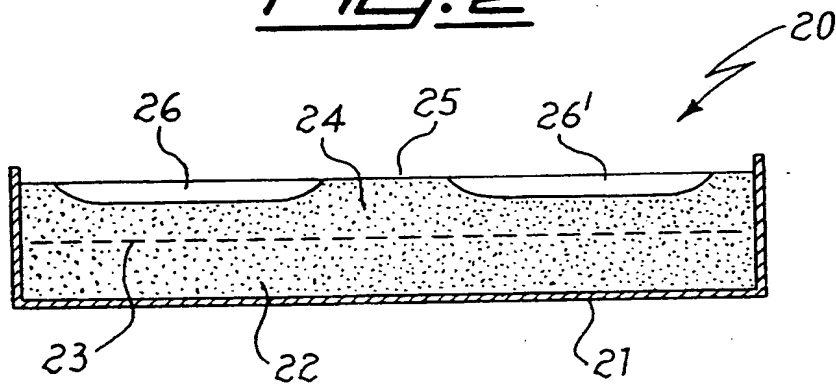


Fig. 4

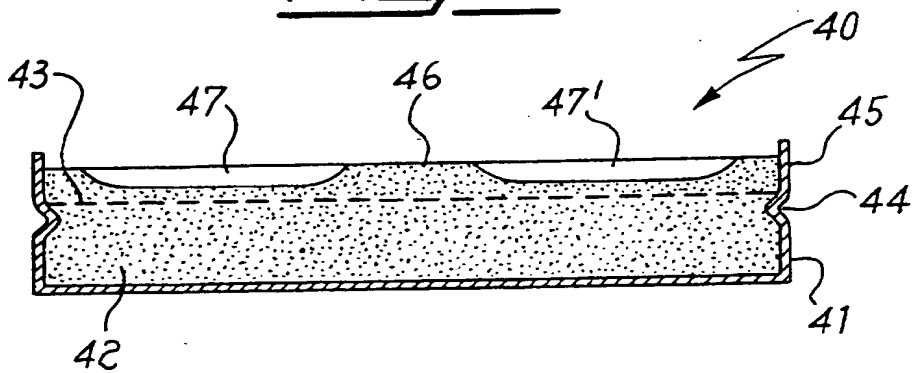




Fig. 3a

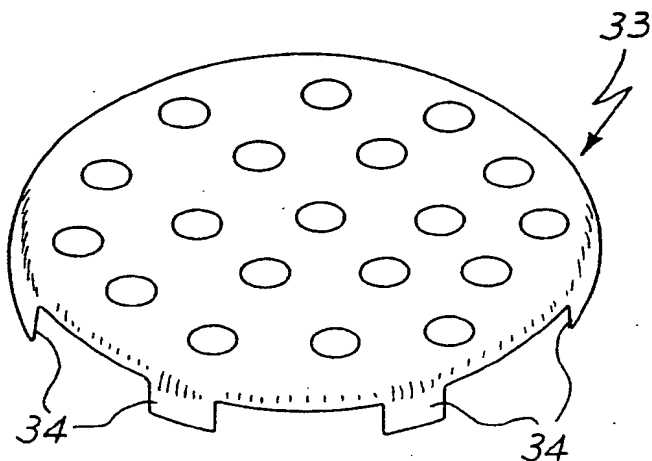
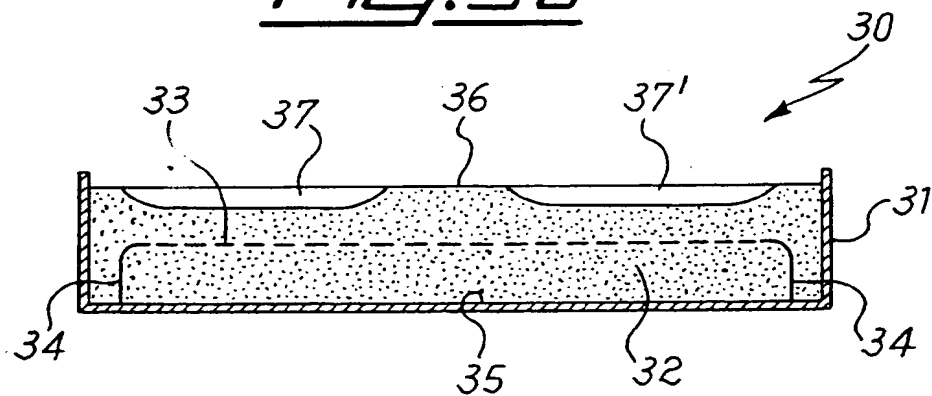
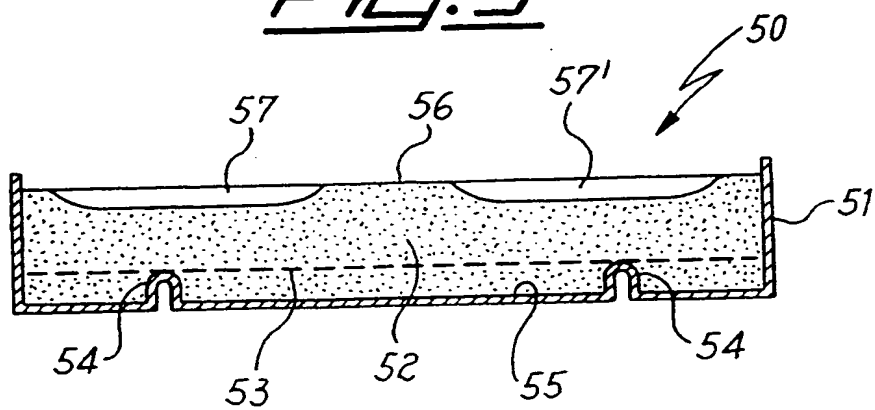


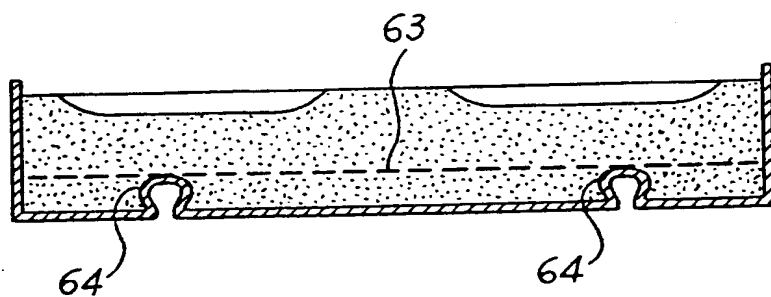
Fig. 3b



**Fig. 5**



**Fig. 6**





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## EUROPEAN SEARCH REPORT

Application Number  
EP 97 83 0748

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	WO 89 10627 A (GETTERS SPA) * page 4, line 1-25 *	1	H01J7/18
Y	US 3 560 788 A (REASH CLAIR ET AL) * claims 1,4 *	1	
A,D	US 3 558 962 A (REASH CLAIR W) * claim 1 *	1	
A	US 3 428 168 A (REASH CLAIR W) * claims 1-12 *	1	
A	EP 0 036 681 A (PHILIPS NV) * claims 1-13 *	1,15	
A	US 3 737 709 A (HORNMAN J ET AL)		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)  H01J
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>25 March 1998</b>	Examiner <b>Van den Bulcke, E</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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